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DIAGNOSTIC LIMITS OF PHENOMENOLOGICAL KINETIC MODELS INTRODUCING THE ACCOMMODATION FUNCTION

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Applicability of macroscopically centered and microscopically localised measurements of solid-state reactions is discussed but their mutual correlation is found difficult. The wellknown models based on the geometrical representation of heterogeneous reactions are analysed with respect to the simple classical model of reaction-order introducing a multiplication function called the accommodation function. The resulting exponents become dependent on the system geometry and are further altered by the system nonideality due to the particles polydispersity, nonregular shapes, nonequal distribution etc.

Classical reaction kinetics has been found to be unsatisfactory when the reactants are spatially constrained on the microscopic level by either walls, interfaces, dislocations or force fields. This is because the most universally found instruction in chemical kinetics "to stir well" is not applicable for reactions in or on media that are solid, viscouos, porouos or otherwise structured. In the absence of convective stirring there is still diffusive homogenisation which however, under dimensional (surface reactions) or topological (solid-state reactions) constrains, is often inefficient. The new theories were needed to explain the results of experiments and computer simulations of reactions that were confined to low dimensions or fractal dimensions or both [1]. Diffusion-controlled reactions with geometrical constrains, as found in heterogeneous kinetics, may thus be described by reactions on fractal domains the hallmarks being the anomalous reactions orders and time-dependent reaction rate constants. These anomalies stem from the nonrandomness of the reactant distributions. Among the practical examples of this fractal-like kinetics are chemical reactions in pores of membranes, excitation trapping in molecular aggregates, fusion in composite materials and particularly the processes in porous (Vycor) class assuming possible controversy about its pore topology [2].

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It is clear that a generalised approach is also needed to be introduced to the long ago developed field of solid-state reactions [3]. Their formulation on basis of well defined but rather simplified geometrical bodies (mostly spheres) is, however, far from the use of above mentioned framework of fractal-like kinetics. Nevertheless we can approach such a solid-state kinetics as a distorted case of homogeneous kinetics where we give a certain geometrical representations to original nondimensional reacting species (molecules) and where the initial conditions (which are usually of little importance in the homogeneous rerandomizing classical kinetics) become indispensable. Similar results of anomalous reaction orders and time-dependent rate constants are expected.

Centered versus localised measurements

Most thermophysical measurements [3] are based on the detection of an averaged property representing the sample state, e.g., DTA, TG, XRD, magnetometry. The other techniques consist of localized measurements at a precise spot on the sample surface such as traditional morphology measurements, e.g., light or electron microscopy, see Table 1. The existence of two kinds of observations, which are difficult to correlate, often leads to contradictions between individual results [4, 5]. This is particularly important in studies directed to heterogeneous kinetics where the averaged data on the degree of reaction a and thus derived phenomenological kinetic models are often criticised for the apparent lack of physical meaning. Moreover the macroscopically determined a using a particular form of centered measurements may not attribute to the same microscopical process as shown e. g. in our previous communication [6] for the crystallization of a chalcogenide glass simultaneously investigated by DTA, XRD and electric resistivity. On the other hand the morphological kinetic information can equally be questioned as being based on a very localized surface pattern which represents a negligible part of the sample and is observed under conditions much different from those occurring during the entire reaction. Moreover electron beams can locally damage the analysed structure as was recently demonstrated by the re crystallization exhibited during prolonged measurements of a well defined silica glass [7], see Fig. 1.

The correct evaluation of kinetic parameters comes from an appropriate estimation of this micro-model of reaction mechanism and its correlation to the as-received macro-process [8] being experimetally determined as a measured response of the sample physical properties to the externally applied experimental conditions [3, 8]. Both isothermal [9] and nonisothermal [3] treatments are based on a geometrical description of the reaction [9] represented by time development of the centered value a yielding an analytical form of a model function which is usually simplified to a formal function supposed to possess a more general validity [3]. In the most simplified case it leads to the reaction-order model which has long been traditional in homogeneous-like kinetics but is often discouraged for heterogeneous kinetics involving solids [3]. Therefore it is of interest to analyze the diagnostic limits of this most simple model by assuming different forms of a multiplying function $h(a)$ introduced to comply with more complex reaction mechanisms [10, 11].

Heterogeneous kinetics assumed as a distorted case of simple homogeneous kinetics

It is well known that a basic form of a kinetic equation exhibits a direct proportionality between the reaction rate ($\mathrm{d}a/\mathrm{d}t = \dot{a}$) and the multiple of two mutually independent functions, $k(T)$ and $f(a)$, called respectively the Arrhenius (exponential) rate constant and the phenomenological (derivative) model of reaction mechanism (where a and T are conventionally the reaction extent and temperature).

In the most traditional case of homogeneous kinetics the $f(a)$ function has the common form of $(1-a)$ if equal amount of chemical species react in a fluid mixture. Assuming $(1-a)$ to be the easiest function to represent the simplest chemical case, any additional complication due to a more complex reaction mechanism can be understood as a deviation from "ideality". It can be quantified by the introduction of a multiplication function called the accomodation function $h(a)$ [10, 11].

$$f(a) = (1-a)\,h(a)$$

Let us now analyse possible ways to express $h(a)$ analytically:

(i) If $h\ (a)$ bears an exponential form of $(1-a)^{n-1}$ it complies with the reaction order model where $n > 1$ [3] (abbreviated as RO) derived for reactions between multiple chemical species in fluid mixture.

(ii) If a chemical reaction takes place in a heterogeneous system, the geometrical limits become dominant and control the $h(a)$ function. For a hypothetical description of a solid-state reaction we have to presume reacting particles of certain dimension instead nondimensional chemical species.

Table 1 The study of solid-state reactions

AVERAGED (centered) measurements		← ? – – – – – – – ? →	LOCALISED (spot) observations	
phenomenological description, (a)			topological (structural) description	
(thermodynamic)	(kinetic)	(study)	(crystallographic)	morpholiogical)
EMF, calorimetry	thermal analysis ($\dot{T}$ = const)	thermophysical measurements	structural measurements (XRD, NMR, etc.)	microscopy
phase stability	phase trasitions ($\dot{a}$)	flux properties	structure, composition	surfaces, morphology
equilibrum	formal kinetics $f(a)$	balance relations	crystalchemistry	interface chemistry
phase diagrams	equilibrium background	gradient theory		
{metastability, kinetic phase diagrams, glass formation, noncrystallinity}				

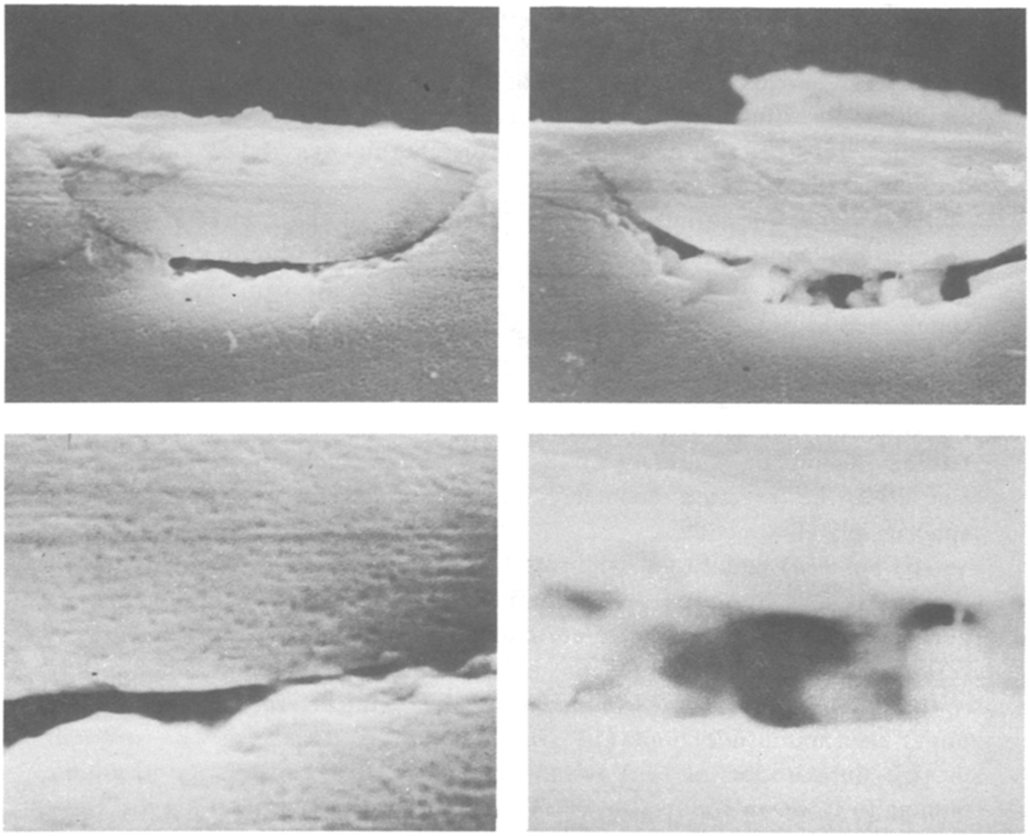

Fig. 1 An illustrative example of the surface alternation caused by electron beam during SEM. The pictures (where bottom raw shows enlarged central area) were provided by courtesy of Dr. K. Jurek (Institute of Physics) and measured on the samples of phase separated silica glass [7] having crystallization temperature about 780°C and melting above 1200°C. The glass was subjected to SEM using the electron beam diameter of about 6 μm and intensity 2.10^{-8} and 7.10^{-8} A at 20 kV, which should theoretically create a temperature increase of about 20 and 70°C, respectively. The first picture demonstrates a mere inpact of electron beam to cause the formation of a crack due to mechanical tension caused by a temperature change. The second one obtained for the higher intensity shows in the same time crystallization along the interface area as well as the remelting of the inner part (as confirmed by dissapperance of liquation spots characteristic for the phase separated glass, as can be seen in the previous case). It follows that actual temperatures can exceed the usually predicted ones being thus dangerous for the conventional scanning procedures.

The resulting phase-boundary reaction then takes place along interfaces propagating inwards to the center ($r \rightarrow 0$) of prolonged cylinders ($2\pi r$) or spheres ($4\pi r^2$) yielding exponential power $n < 1$ (i.e. ½ and ⅔ respectively). This represents two dimensional (lamillar) and three dimensional (globular) heterogeneous system where the interfaces are taking the role of concentrations.

(iii) The above discussed models of so called shrinking-core particles can be limited by diffusion to or from the reaction boundary leaving the reaction rate inversely proportional to the diffusion thickness layer and usually decreasing the exponent n by half.

(j) Another important step is the formation of the first interface (i.e. geometrical embryos of the growing phase). If the $h(a)$ function is expressed in the form of $[-\ln(1-a)]^p$, different values of the exponent p express simultaneous processes of formation and growth of new phase particles within the original matrix phase. The values of p reflects the dimensionality, nucleation rate and phase-boundary or diffusional mode of the process, and the function $f(a)$ assumes the traditional form of the John-Mehl-Avrami-Erofeev-Kolmogorov (JMAYK) [3, 9] equation. Such an approach again simplifies the reaction geometry into the idealised system of growing spheres, plates or needles.

(jj) For $h(a)$ equal to a^m the $f(a)$ function assumes a particular form of the Šesták and Berggren (SB) equation [12]. Although it exhibites a most general use it bears only little correspondence to the popular geometrical representation of a heterogeneous system under investigation and similarly to the reaction-order model (where $n < 1$) bears uncertainty of its definition under zero and infinity limits [13-15].

(jjj) Substitution of $h(a)$ by an exponential function brings problems similar to those introduced by $k(T)$ resulting in the so-called kinetic compensation effect [16, 17] which has not been solved as yet [3].

The applicability of three basic kinetic models and their geometrical representation

Figure 2 illustrates the theoretical relationship of the individual types of the functions $h(a)$ in a three dimensional representation of n and a. It follows that the RO model is a monotonously decreasing function while the JMAYK and SB models exhibit extremes characterised by the distinct number of inflection points [18]. This may help to distinguish the possible utilizability of individual forms of $h(a)$ in the order of complexity from (i) to (j). Assuming the mathematical behaviour of the basic equation for derivates $\dot{a}$ and $\ddot{a}$ when equal to zero, see table under Fig. 2, the plot a *vs.* $\dot{a}$ can be used to check the type of curvature. If there is a maximum which coincides with $a_{\text{stat}} = 0.63$, the JMAYK model can be used while for $a_{\text{stat}} << 0.6$ the SB model is more suitable [18]. For a more complex case we can introduce a second exponent and we can formally describe any type of a reaction by the combination [12]:

$$(1-a)^n\, a^m$$

$$(1-a)^n\, [-\ln(1-a)]^p$$

Correlation of hypothetical models with actual processes

It is understandable that the above discussed types of the accommodation function are difficult to relate to a particular reaction mechanism. On the other hand a given function *h(a)* can well satisfy the phenomenological course of any reaction path, even for complex solid-state processes. In order to include the reality of a system investigated we have to consider [10, 11], cf. Fig. 3.:

(i) Spheres polydispersity (where the greater spheres evidently exhibit a prolonged reaction time yielding a discrepancy in decay periods).

(ii) Nonequal and nonregular shapes which do not correspond to the conventional globular geometry (fortunately a kind of similarity law is valid for geometrically similar bodies, the largest particle dimension being again responsible for a prolonged reaction time).

(iii) Particles shielding and overlapping (particularly effective in nucleation-growth processes of new phase formation within the original matrix phase).

(j) Unequal mixing of starting components (rising from either mechanical or segregation phenomena providing a localised basis to ease the formation of intermediate-metastable phases later to decompose to equilibrium products) [8]

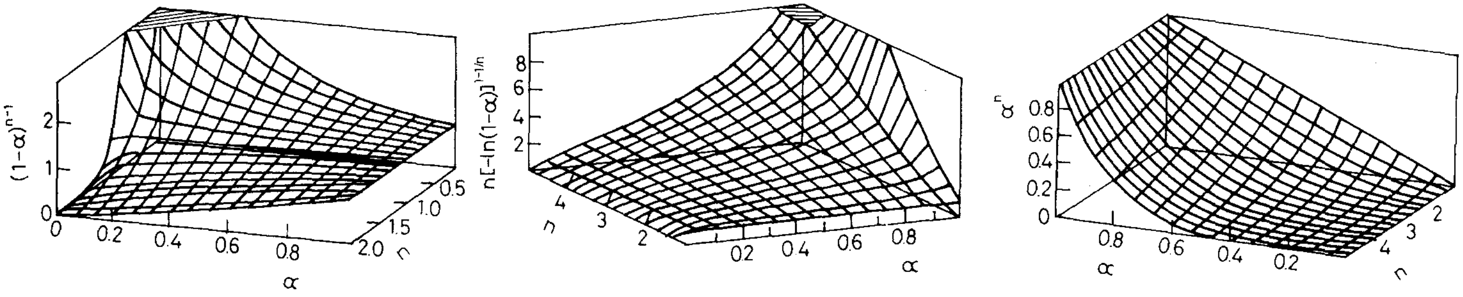

Fig. 2 Three-dimensional representation of the accommodation function $h(a)$ for the normalised value of the extent of reaction (a) and the exponent n, which is equal to n (for RO model), to $1/(1-p)$ (for JNAYK model) and to m (for SB model), *including the list of basic functions* derived by individual mathematical operations.

Model:	RO:	JMAYK:	SB:
$\int_0^a \mathrm{d}a / f(a) = g(a)$	$[1-(1-a)^{1-n}]/(1-n)$	$[-\ln(1-a)]^{1-p}$	no analytical form
$f(a) = (1-a)\underline{h(a)}$	$(1-a)^n$	$(1-a)[-\ln(1-a)]^p/(1-p)$	$(1-a)a^m$
$\mathrm{d}f(a)/\sqrt{x}\,\mathrm{d}a = F(a)$	$n(1-a)^{n-1}$	$n[-\ln(1-a)]^p-(n-1)[-\ln(1-a)]^{p-1}$	$a^m-ma^{m-1}(1-a)$
$F(a)=0$	non	$a_{\mathrm{stat}} = 1-\exp(-p)$	$a_{\mathrm{stat}} = m/(m+1)$
$\mathrm{d}F(a)/\mathrm{d}a=0$	non	non	$(m-1)/(m+1)$
$\mathrm{d}\ln f(a)/\mathrm{d}a = F\ln(a)$	$n/(1-a)$	complex	$[a(m+1)-m]/[(1-a)a]$
exponent	non	$p=1/[1+\ln(1-a_{\max})]$	$m = a_{\max}/(1-a_{\max})$

(jj) Topochemistry and morphological preference to easy reaction paths (interface curvature and crystalographic orientations).

For the well known case of growing nuclei, the overlapping effect is compensated for by a function in the form of $(1 - a)$ which multiplies the reaction rate a and which results in changing the exponent m of the logarithmic function in the JMAYK equation. Probably we can expect a similar compensation effect when changing an exponent to adjust the $h(a)$ model to real conditions of a reaction under study as listed from (i) to (j).

Discussion

It is clear that the present state of art of kinetics as applied to solid-state reactions is not appropriate to sophisticated means available in solid-state chemistry [19, 20]. There are some nontraditional new approaches [1, 8] but the linkage of most treatments to the traditional geometrical description is very firm and hard to overcome. The use of phenomenological models has been critizised [13-18] but unified methods newly suggested [10, 11, 18] helps again to mere characterization of the extent of complexness of the formal functions conventionally utilized. Therefore we can merely distinguis proportionable relevancy of the individual RO, JMAYK and SB models to match with the gradual increment of complexity of an experimentally determined kinetic curve representing the course of the reaction in question. There, however, is still missing a correlation between the microscopic process (detectable only locally under not well guaranteed conditions) and macroscopic process (capable of measuring "in situ" even at increased temperatures).

Stereology seems be a powerful tool for a future description of processes when examining its microstructure with the aid of a computer. Multiple scanning and summation of the morphology, views in different sections may provide us the three basic features, cf. Fig. 3 [21]. It can be:

(i) the characteristic dimension giving idea about either shortest or longest particle size,

(ii) average boundary line surrounding particles which gives upon the summation an idea about their characteristic surface and

(iii) mean section area of particles exhibiting upon the summation a characteristic particle volume.

Altogether they can provide basis how to estimate "characteristic particle geometry" and to correlate it to the idealized shapes using similarity laws.

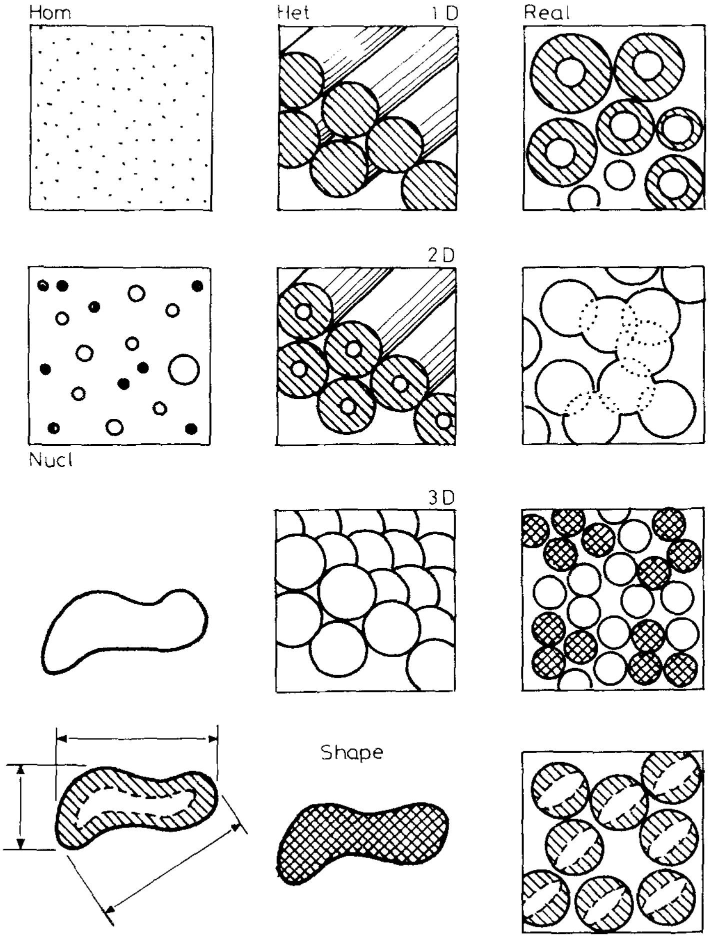

Fig. 3 Schematic diagram of a hypothetical shift of the system geometry from the homogeneous model to the idealised heterogeneous model upon the introduction of dimensionality (second cullom) where the kinetic description changes from the concentration dependent to that of the surface-to-volume dependent. Modelling of the kinetic behaviour of real particles when assuming polydispersity, overlapping, unequal mixing and nonisotrophy (third cullom, upper down) is very difficult and not fully appreciated. The introduction of still further complication: the particle nonsphericity (see buttom), is necessary to match the real morphology views but uncommon as yet. For the sake of illustration the original and reacted parts are distinguished by hatching

Namely important is the ratio of mean particle surface and volume which become responsible for the true reaction progress. It, however, would certainly need an increased effort for united approaches by solid-state chemists, experimental physicists and statisticians giving basis for a desired interlinking between the centered measurements of *a* and the localized determination of morphology of reacting particles.

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Zusammenfassung — Es wird die Anwendbarkeit von makroskopisch zentrierten und mikroskopisch lokalisierten Messungen von Festphasenreaktionen beschrieben, jedoch wurde ihre Korrelation als kompliziert befunden. Diese wohlbekannten Modelle, die auf einer geometrischen Darstellung heterogener Reaktionen beruhen, wurden ausgehend von dem einfachen klassischen Reaktionsordnungsmodell unter Einführung einer als Anpassungsfunktion bezeichneten Multiplikationsfunktion untersucht. Die resultierenden Exponenten hängen nunmehr von der Geometrie des Systemes ab und werden weiterhin von der Nichtidealität des Systemes (Polydispersität der Partikel, unregelmäßige Formen, unregelmäßige Verteilung usw.) beeinflußt.